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Impact of Particle Size and Agglomeration on Settling of Solids in Continuous Melters Processing Radioactive Waste Glass

Prepared for the U.S. Department of Energy
Assistant Secretary for Environmental Management

Office of River Protection

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Impact of Particle Size and Agglomeration on Settling of Solids in Continuous Melters Processing Radioactive Waste Glass

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Abstract

The major factor limiting waste loading for many waste compositions in continuous waste glass melters is the settling of crystalline materials. The currently used constraints, i.e., the minimum liquidus temperature or the maximum fraction of equilibrium crystallinity at a given temperature, are based on thermodynamic equilibria. Because of the rapid circular convection in the melter, these constraints are probably irrelevant and cannot prevent large crystals from settling. The main factor that determines the rate of settling of individual crystals, such as those of spinel, is their size. The tiny crystals of RuO_2 are too small to settle, but they readily form large agglomerates that accelerate their rate of settling by several orders of magnitude. The RuO_2 agglomerates originate early in the melting process and then grow by the shear-flocculation mechanism. It is estimated that these agglomerates must either be of hundreds micrometers in size or have an elongated shape to match the observed rates of the sludge-layer formation.

PACS: 47.57.ef, 81.05.Kj, 81.10.Fg

1. Introduction

Three requirements drive and constrain the radioactive waste glass technology [1]: 1) to produce glass that is sufficiently resistant to corrosion by water to meet required

regulations and thus can be accepted for long-term disposal, 2) to maximize the waste content in the glass (the waste loading), and 3) to formulate glass that is easy to process with the available technology. For wastes containing large fractions of components that are sparsely soluble in glass, a worry that undissolved solids may settle and accumulate in the continuous melter conflicts with the effort to maximize the waste loading [2].

Sparsely soluble components begin to dissolve in the melter feed, a mixture of waste and additives, at early stages of feed-to-glass conversion. Melter-feed components are of various kinds, such as inorganic salts, refractory oxides, amorphous gels, organics, etc. At elevated temperatures, most of the feed components react to form glass melt or dissolve in the glass melt that has been formed. With a few exceptions, inorganic salts, such as nitrates, nitrites, and carbonates, are the first to react with glass-forming additives, such as boric acid and silica. Sulfate that tends to segregate on top of the melt [3] and molybdate [4] that tends to sink to the bottom are two exceptions. On the other hand, refractory components, initially present as oxides, hydroxides, oxyhydroxides, and salts, gradually dissolve in the early borosilicate melt or react with each other to create secondary crystalline forms, such as various spinels [5,6], zircon [7], or alkali and earth alkali zirconium silicates [8,9]. These complex oxides eventually dissolve in glass, unless the glass temperature is below the liquidus. Oxides of noble metals form a special category. Their solubility in glass is extremely low. Oxides of Rh and Pd easily reduce to metals, though oxides of Rh and Ru are also compatible with spinel [10]. However, most Ru survives as RuO_2 [11].

The most common and potentially bothersome sludges that can accumulate in continuous melters vitrifying high-level radioactive wastes are spinel, RuO_2, and their combination. Figure 1 shows an example of RuO_2 needles connecting crystals of spinel [12]. A sludge layer can possibly clog the melter discharge, but it can also be electrically conductive and distort the electric field within the melt (electric conductivity data exist for RuO_2 sludge [13], but not on spinel sludge or sludge that combines RuO_2 and spinel).

Spinel crystals are more or less evenly distributed within the melt, depending on the feed homogeneity and the impact of the velocity and temperature fields on their distribution. Therefore, spinel usually settles as individual crystals. However, RuO_2 has a strong tendency to form agglomerates. This contribution provides a review and discussion of what is known about settling of these two types of solid phases, i.e., settling of individual crystals of spinel and settling of crystal agglomerates of RuO_2.

2. Settling of Individual Crystals

To avoid or minimize the settling of crystalline phases in melters, glasses have been formulated either with a constrained liquidus temperature, T_L [14], or the temperature T_1 at which the equilibrium fraction of solids in the melt is below a certain value, e.g., 1 vol% [15]. The reasoning behind these constraints is that if T_L or T_1 are high enough, crystals would not exist in molten glass in the melter or would be present in concentrations low enough to prevent any significant settling during the melter lifetime.

However, this reasoning is objectionable, at least for spinel, a common crystalline phase existing at processing temperatures of radioactive waste glasses [16]. Spinel crystals enter the melt from the cold cap (the melter feed in the process of being converted to molten glass and floating on the pool of molten glass in the melter) where they are formed by reactions between the feed components [17,18]. Unless the waste loading in the glass is very low, or the waste does not contain spinel-forming components at high concentrations, spinel crystals enter the melt ~100°C below both T_L and T_l. According to the assumption on which the T_L and T_l constraints are based, crystals dissolve as soon as the melt temperature increases above the T_L. In other words, it is assumed that the melt is at, or close to, phase equilibrium, or that the time required to reach equilibrium is short as compared to the characteristic time of the melt circulation in the melter. This assumption is unjustified because the rate of crystal dissolution is slow [5,19] as compared to the time the melt from the cold cap needs to reach the melter bottom.

Indeed, computer models show that all-electric (Joule-heated) radioactive-waste-glass melters are nearly perfect mixers [20]. This is because the circulation velocity of the melt, driven by the temperature differences between the melt below the cold cap and the cold-cap bottom, is orders of magnitude higher than the throughput velocity, which is determined by the generally slow rate of conversion of melter feed to molten glass [21,22]. Moreover, in melters developed for the Hanford Waste Treatment and Immobilization Plant, the intensity of circulation flow is greatly enhanced by bubbling [23]. Hence, the rapid circulation currents bring crystals to the melter bottom soon after they enter the melt. Even though the melt temperature increases during the passage from

the cold cap to the bottom, the time does not allow the crystals to approach equilibrium with the melt. Unless they are extremely small, i.e., having a large surface-to-volume ratio, they are carried close to the bottom virtually intact.

Crystals that come sufficiently close to the melter bottom settle and form a layer of crystalline sludge. Once created, the sludge cannot be easily dissolved. Crystals in the sludge can undergo Oswald ripening, but cannot dissolve even when the temperature is increased because the melt within the sludge layer is saturated, and its T_L is low.

The rate of settling can roughly be assessed from the Stokes equation that estimates the velocity at which crystals move in the direction of the gravity vector. The sludge-layer growth rate increases in proportion to this velocity, even though the melt velocity parallel to the bottom surface causes the sludge layer thickness to vary (a snowdrift effect). For non-agglomerating crystals, the main parameter that determines the rate of settling is the particle size because, by the Stokes equation, the settling velocity is proportional to the square of the particle effective radius. For example, 100-μm crystals settle 10,000 times faster than 1-μm crystals. A simple calculation estimates that the rate of the sludge growth from micron or submicron spinel crystals would be merely a few micrometers per year [24], regardless of the T_L.

A mathematical model has been created that can handle not only the fluid dynamics of continuous electric melters, but also the behavior of spinel crystals in the melt, including their dissolution, growth, and settling [25]. According to more precise calculations that

this model allows, the rate of settling increased with the crystal size to the power of 2.3, which was higher than the 2 predicted by the Stokes equation [16]—see Figure 2. This amplified impact of crystal size on the rate of settling was caused by crystal dissolution that affects small crystals more than large crystals.

As Figure 2 demonstrates, the T_L had little impact on the settling rate of 100-μm spinel crystals and mildly influenced the settling rate of crystals <100 μm, even though the T_L varied from 978 to 1178°C, i.e., both below and above the nominal melter operating temperature of 1150°C (the rate of settling of 1-μm crystals increased 18 times, from 11 μm/year to 200 μm/year, when the T_L increased from 978°C to 1178°C, but only by 16%, from 1.4 m/year to 1.6 m/year, in response to the same change in T_L when the crystal size was 100 μm). Thus, the sludge-layer grew even when the temperature of the bulk of the melt in the melter was above the T_L. While virtually unrelated to the T_L, crystal size appears to have a decisive influence on the sludge-layer-growth rate. Even in glass formulated for a spinel-forming waste with the T_L above the average melt temperature, 100-μm particles will hardly get smaller before they reach the melter bottom, where they settle, whereas 1-μm particles settle so slowly that they will be nearly all removed from the melter with the glass even if their T_L were lower than that of the melt anywhere in the melter.

While the nucleation and growth of spinel crystals from the glass melt is well understood, the mechanism of their formation within the cold cap it is not clear, and the existing mathematical model [25] cannot predict the size of spinel crystals entering the melt from

the cold cap. Spinel forms within the cold cap by precipitation from molten salts [18] or by reactions between spinel-forming components dissolved in molten glass. Experimental studies show that spinel precipitates from molten salts in the form of mostly submicron octahedrons [18] that later dissolve in alkali-rich early glass-forming melt. As the melt becomes gradually more acidic, spinel precipitates again, forming octahedrons that are larger than those from the molten salt—see Figure 3; only exceptionally do spinel crystals form twins or exhibit dendrite-like growth as seen in Figure 3. Spinel crystals often form in the melt as a reaction between the fast-growing crystals of hematite and spinel-forming oxides dissolved in the melt (NiO, Cr_2O_3, MnO, ZnO, etc.) as seen in Figure 4. These crystals are close to each other, forming two-dimensional clusters (hematite crystals are thin platelets).

Spinel crystals are more numerous and grow smaller if heterogeneous nucleation sites abound. Sites for spinel nucleation are provided by oxides of Ru, Pd, and Rh; Figure 5 shows the effect of Pt on the number density of spinel crystals (other noble metals have similar influence). Apart from being nucleation agents, noble metals do not influence the equilibrium fraction of spinel in the melt. Noble metals are generally present in radioactive wastes in concentrations sufficient to nucleate enough crystals of spinels to limit their growth to a size of approximately 1 μm [5].

Aside from crystal size, a few other variables affect the rate of spinel settling. The most obvious is the particle nonsphericity [26,27]. Hindered settling is caused by simultaneous settling of multiple particles [28]. Unless trapped in high-viscosity inhomogeneities [29],

spinel does not readily form agglomerates. However, the distribution of spinel crystals in the melt is usually nonuniform even after the feed has been thoroughly homogenized and the glass is milled and remelted. Spinel formation involves diffusion and reduction-oxidation and often proceeds through intermediate crystallization of hematite [30] (Figure 4). It is likely, though not proven, that loose groups of spinel crystals sink faster than individual crystals.

The worry about excessive settling of crystalline phases in waste glass melters was a response to experiences with nonradioactive melter testing that is commonly performed with waste simulants without additions of expensive noble metals (i.e., Ru, Pd, Rh). Not surprisingly, because of the lack of nucleation agents that noble metals provide, spinel crystals that form during these melter tests are not numerous and, therefore, grow large. Spinel crystals rapidly settle and make a thick layer of bottom sludge that is found in these melters at the end of even short-term tests [31-34]. Projections of this rate of settling on a large-scale melter, which is expected to operate for several years, leads to an alarming conclusion that the melter could be blocked by spinel in a few months unless the waste loading is drastically reduced. But a test with noble metals would reveal that such worries are not substantiated, and the waste loading may be limited by other requirements than the T_L or T_1 constraints.

3. Settling of RuO_2

Ruthenium dioxide is a special case. Unlike spinel, RuO_2 particles have a strong tendency to agglomerate. Ruthenium is dissolved in the nitrate form in the molten ionic salt

mixture that forms early in the melting process [35]. RuO_2 typically forms needles that precipitate from molten salts as well as from glass melt. Molten salts decompose and react with feed solids at the early stages of the melting process. As the pockets of molten salts shrink in the reacting feed, RuO_2 needles precipitate and agglomerate. Some RuO_2 dissolves in the early high-alkali glass-forming melt and later precipitates in the form of needles as the fraction of glass formers, such as silica, alumina, and zirconia, increases, and the melt basicity decreases. Once in the melt, RuO_2 needles readily agglomerate by shear flocculation [36]. Basically, particles (crystals and their agglomerates) that move on parallel streamlines with different velocities in a liquid subjected to a high shear, and thus experience steep velocity gradients, inevitably bump into one another and remain connected. This way, ever larger agglomerates are built. This mechanism applies to RuO_2 particles of any shape (e.g., when solid RuO_2 is added to the feed simulant instead of as a nitrate compound, the particles have three-dimensional irregular shapes). Large RuO_2 agglomerates were observed in laboratory crucibles where the melt is subjected to extreme velocity gradients in the menisci that the melt makes with the crucible walls (a powerful convention in these menisci is driven by the surface tension gradients [37]).

The density of the agglomerates falls between the density of the crystals and the melt:

$$\rho_A = C_S \rho_S + C_M \rho_M \qquad (1)$$

Here ρ is the density, C_I the average I-th phase volume fraction in the agglomerate, and the subscripts A, M, and S denote the agglomerate, solid, and melt, respectively ($C_M + C_S = 1$).

We will assume here, for simplicity, that the melt in agglomerates is immobilized and, hence, an agglomerate behaves as a solid particle (for a better approximation, we might treat agglomerates as "porous" particles [38]). The driving force for settling of a single solid particle is the density difference, $\Delta\rho = \rho_S - \rho_M$. For an agglomerate, by Equation (1), the driving force is the difference $\rho_A - \rho_M = C_S\Delta\rho$.

Although RuO_2 agglomerates may have a low density (typically, C_S is in the range from 0.05 to 0.17 [39]), they still can fall with a high velocity because of their large size. Ignoring the non-sphericity of both agglomerates and single particles, neglecting the hindered-settling effect, and assuming that agglomerates are equal in volume and solid concentration, the ratio (ζ) of the sinking velocity of an agglomerate, v_A, to the Stokes velocity for a single particle, v, is

$$\zeta = v_A/v = C_S(d_A/d)^2 \qquad (2)$$

where d_A is the effective diameter of an agglomerate, and d is the effective diameter of a single particle (by the Stokes equation, the particle velocity is directly proportional to the square of the particle diameter).

Data on RuO_2 agglomerates in laboratory crucibles and experimental melters are summarized in reports by Elliott et al. [11] and Cooper et al. [39]. With $\rho_S = 6.97\times10^3$ kg/m^3, $\rho_M = 2.17\times10^3$ kg/m^3 (at 1150°C), and C_S from 0.05 to 0.17, we calculate from Equation (1) that ρ_A varies from 2.41×10^3 to 2.99×10^3 kg/m^3. The typical size of a single RuO_2 crystal was in the range from 0.5 to 1 μm, and the agglomerates were within the range from 10 to 60 μm. Thus, by Equation (2), the velocity ratio, ζ, can vary from 5 to 2500.

The bottom sludge layer growth rate is $v_B = (C/C_B)v_A$, where C is the average volume fraction of solid in the total melt (approximately, the initial RuO_2 concentration in glass, provided that the dissolved fraction of RuO_2 is negligible), and C_B is the volume fraction of RuO_2 in the sludge. A typical mass fraction of RuO_2 in glass is 1.8×10^{-4}. The corresponding value of C is 5.6×10^{-5}. With $C_B = 0.06$ [40], $C/C_B = 9.3\times10^{-4}$, and v_B/v can vary from 0.005 to 2.3 (agglomerates can contain more RuO_2 than the bottom sludge because of the loose packing of the agglomerates when they settle). According to Cooper et al. [39], $v = 6\times10^{-10}$ m/s. Accordingly, the sludge-layer growth rate can vary between 2.8×10^{-12} m/s and 1.4×10^{-9} m/s, depending on the size of the agglomerates. The rate of the sludge-layer growth, thus, would be in the range from 0.09 to 43 mm per year. If only individual crystals were settling, the sludge layer would grow at 0.0018 mm per year.

In a recent study [40], a thorough model analysis of an experimental waste-glass melter was performed. A glass contained 0.09 mass% of RuO_2 ($C = 0.0003$). The crystals were rods of 0.7 μm in diameter and 0.5 to 21 μm long. It was assumed that RuO_2 crystals do

not agglomerate and settle as individual particles. Unsurprisingly, the results showed that all RuO_2 would be discharged from the melter with the glass. This result was at variance with the measured extent of settling that was 1.3 kg of RuO_2 settled during 2200 minutes of the test (estimated from the mass balance). Provided that $C_B = 0.06$, the average sludge layer thickness grew at the rate of ~0.2 m per year. Schill et al. [40] achieved agreement with the experimental findings only when they assumed that all RuO_2 would be removed from the melt into the sludge from within ~1 mm "entrapment" distance from the sludge surface.

A simple calculation shows that the experimentally determined rate of RuO_2 settling would occur if the RuO_2 agglomerates were >100 μm. Such agglomerates were seen in German glasses [13] and in crucible melts of high-alumina (10 to 19 mass% Al_2O_3) glasses with 0.02 mass% RuO_2 [41]. Their formation can be expected because a fast circulating melt provides a plentiful opportunity for larger agglomerates to contact and attach other agglomerates of similar or substantially smaller sizes. Also, if RuO_2 agglomerates carry heavy spheres of metallic Rh and Pd, or if they carry entrapped bubbles, their velocity differs from other agglomerates of equal sizes, and this can further increase the chance of their coalescence into larger agglomerates. Additionally, melt bubbling creates steep velocity gradients in the melt and thus can accelerate RuO_2 agglomeration. Finally, larger agglomerates have a tendency to move in the direction opposite to the velocity gradient and thus can be subjected to a high frequency of interaction with other particles via the shear flocculation mechanism.

Although agglomeration can account for fast settling, the hypothetical "entrapment" distance from which the agglomerates are swept to the sludge layer can have a physical basis. The steep velocity gradients that exist close to the sludge-layer surface cause the agglomerates to rotate and move in the direction of lower velocities. This increases the chance of agglomerates attaching themselves to the sludge layer. This can be assisted by the irregular shapes of RuO_2 agglomerates and the roughness of the sludge-layer surface. For example, when elongated, or raindrop shaped, agglomerates reach the bottom sludge layer, they may extend "tentacles" that help trap smaller agglomerates that would otherwise not reach the bottom.

A question arises whether it would be possible to prevent RuO_2 crystals from agglomerating. A tempting possibility is to introduce spinel-forming components that prevent RuO_2 crystals from contacting each other (Figure 1). This is unlikely to prevent sludge formation [32,33], but it may slow down the rate of settling. Another possible solution is the periodical removal of the RuO_2 sludge from melters with a funnel-shaped bottom equipped with a drain [13].

4. Conclusion

The main factor that determines the rate of settling of spinel crystals is the crystal size. Large crystals settle rapidly regardless of phase equilibria, but the presence of noble metals in the melter feed prevents the formation of large spinel crystals. The settling of RuO_2 crystals is greatly accelerated by their tendency to form large agglomerates. Whereas spinel can be almost entirely removed from the melter with glass if its crystals

are small, it is probably impossible to prevent RuO_2 agglomeration, and, hence, its settling appears inevitable unless RuO_2 sludge is periodically removed from the melter.

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Figure Captions

Figure 1. Micrograph of spinel and RuO_2 crystals in a HLW [12].

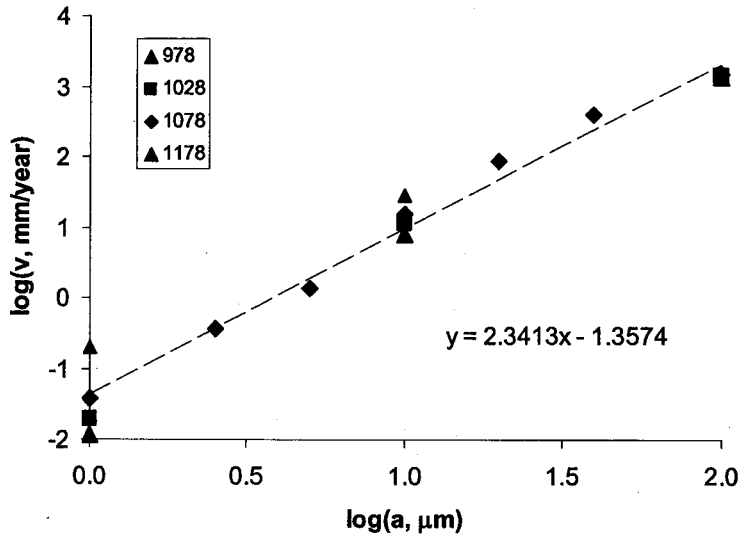
Figure 2. Computed rate of spinel sludge layer growth (v) versus crystal size (a); the legend shows the T_L in °C [16].

Figure 3. Spinel octahedron (top), twin crystal (middle; the size bar indicates 30 μm), and cross-like crystal (bottom).

Figure 4. Crystal of hematite (~300 μm) reacting with melt components to form spinel crystals.

Figure 5. Spinel crystal number density (n_s) as function of temperature for MS-7 glass without nucleation agent additions and with 0.1% Pt [5].

Figure 1.


978
1028
1078
1178
y = 2.3413x - 1.3574
log(v, mm/year)
log(a, μm)
4
3
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1
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-1
-2
0.0
0.5
1.0
1.5
2.0

Figure 2.

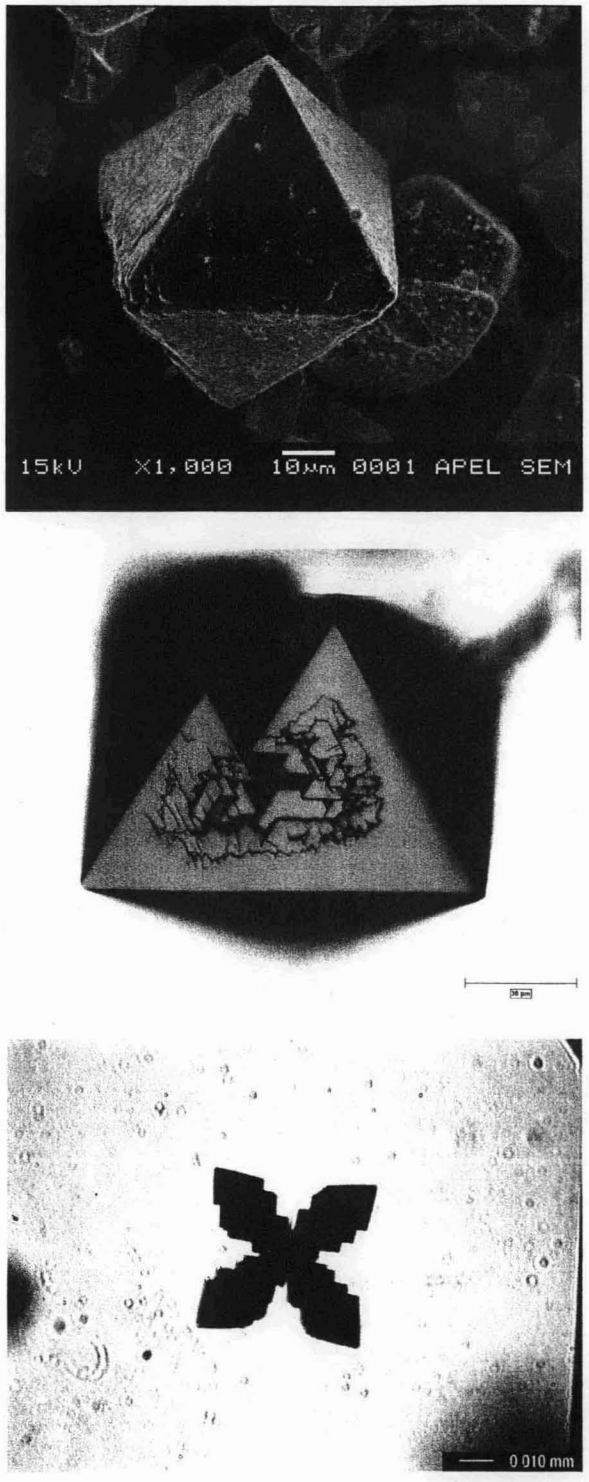

Figure 3.

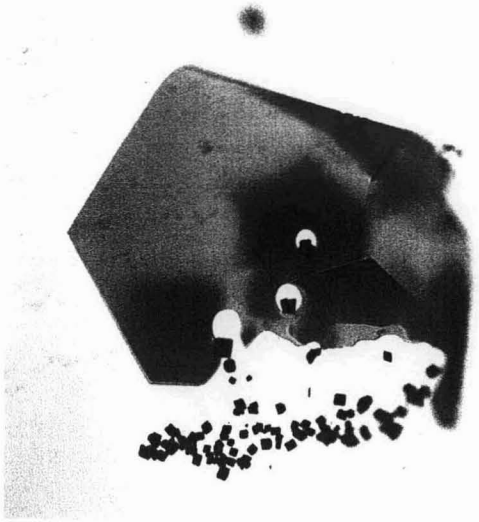

Figure 4.

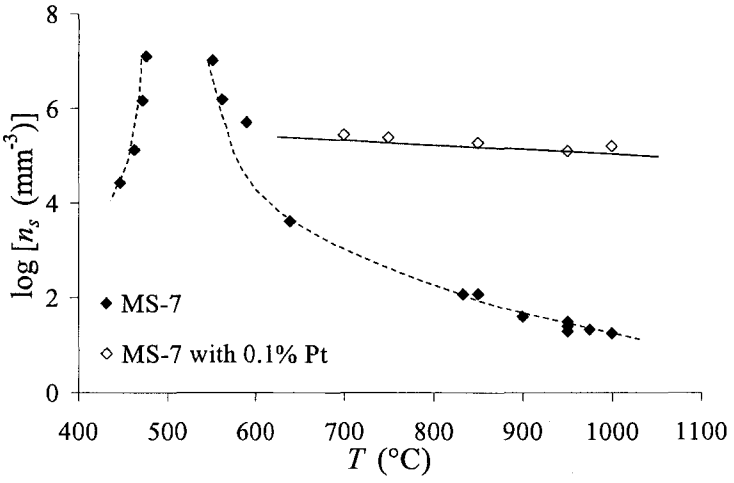
8
6
4
2
0
log [n_s (mm^{-3})]
MS-7
MS-7 with 0.1% Pt
400
500
600
700
800
900
1000
1100
T (°C)

Figure 5.